

The University of Chicago

THE
MOLECULAR REARRANGEMENT OF
2,2-DIPHENYL-2-HYDROXY-
ETHYLAMINE

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

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HERMAN SAMUEL BLOCH

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I. INTRODUCTION

In the course of a study of the rearrangement of trisubstituted methyl hydroxylamines, Maver¹ attempted to prepare methyl-diphenylmethyl hydroxylamine, $\text{CH}_3(\text{C}_6\text{H}_5)_2\text{CNHOH}$, by the action of phenyl magnesium bromide on acetophenone oxime. Contrary to expectation, the rearrangement of the product of this reaction yielded methylimino benzophenone, $(\text{C}_6\text{H}_5)_2\text{C}=\text{NCH}_3$; according to the Stieglitz theory of rearrangements of this type,² phenylimino acetophenone, $\text{CH}_3\text{C}_6\text{H}_5\text{C}=\text{NC}_6\text{H}_5$, should have been formed. In order to explain this discrepancy between theory and fact, the reactions involved in Maver's work were subjected to a more thorough study.

As a result of this further investigation, it was shown by Cole³ that Maver's supposed methyldiphenylmethyl hydroxylamine is actually the isomeric compound 2,2-diphenyl-2-hydroxy-ethylamine, $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})\text{CH}_2\text{NH}_2$. The latter compound was prepared by Cole from phenyl magnesium bromide and glycine ethyl ester hydrochloride, according to the method of Weidenkaff;⁴ and a comparison of the salts and derivatives of the products of the two methods of synthesis leaves no doubt of their identity. Further confirmation has been furnished by Stillson,⁵ who showed that the

¹M. E. Maver, Doctorate Dissertation, University of Chicago, 1926.

²J. Stieglitz, Proc. Nat. Acad. Sc., I, 196 (1915).

³J. E. Cole, Doctorate Dissertation, University of Chicago, 1929.

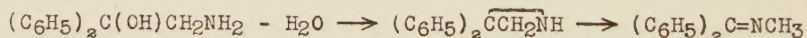
⁴Ber., 38, 1688 (1905).

⁵G. H. Stillson, Doctorate Dissertation, University of Chicago, 1933.

N-methyl derivative of Maver's amino-alcohol is identical with the product of the action of phenyl magnesium bromide on sarcosine ethyl ester hydrochloride. It may be added that methyldiphenylmethyl hydroxylamine has been prepared by Cohn¹ and has been shown to undergo the normal rearrangement, with the formation of phenylimino acetophenone.

Yet to be explained was the nature of the rearrangement by which 2,2-diphenyl-2-hydroxy-ethylamine, $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})\text{CH}_2\text{NH}_2$, is converted into methyliminobenzophenone, $(\text{C}_6\text{H}_5)_2\text{C}=\text{NCH}_3$. Maver, Cole, Lenth,² and Sturgeon³ all found that when the former compound, or its N-benzoyl derivative, is heated with soda-lime or calcium oxide, methyliminobenzophenone is formed in practically quantitative yield; and that, furthermore, the alkamine (as the amino-alcohol will hereafter be called), or its sodium salt, when heated alone, undergoes the same rearrangement. Similarly, Sturgeon showed that 2,2-diphenyl-2-hydroxy-1-methyl-ethylamine, $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})\text{CH}(\text{CH}_3)\text{NH}_2$, undergoes an analogous rearrangement, forming ethylimino benzophenone.

In order to explain the mechanism of the alkamine rearrangement, Stieglitz postulated the formation of unsymmetrical diphenylethylene imine, $(\text{C}_6\text{H}_5)_2\overline{\text{CCH}_2}\text{NH}$, as an intermediate product:



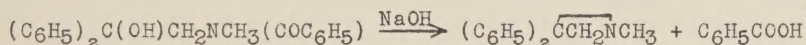
To determine whether ring formation does take place under the conditions of the rearrangement, Lenth heated with soda-lime the

¹M. L. Cohn, Doctorate Dissertation, University of Chicago, 1929.

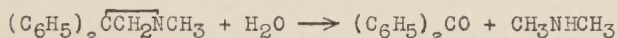
²C. W. Lenth, Doctorate Dissertation, University of Chicago, 1930

³W. E. Sturgeon, Doctorate Dissertation, University of Chicago, 1929.

N-benzoyl derivative of the N-methylated alkamine, $(C_6H_5)_2C(OH)CH_2NCH_3(COC_6H_5)$. He obtained a compound having the empirical formula $C_{15}H_{15}N$, which, upon hydrolysis, formed benzophenone and dimethylamine. The most likely structure in accord with these facts is that of the ring compound unsymmetrical diphenylethylene methylimine, $(C_6H_5)_2\overline{CCH_2NCH_3}$, which would be formed as follows:



This ring, with two phenyl groups attached to one of the carbon atoms, could break at the carbon-carbon bond to form dimethylamine and benzophenone:



The alternate structure $(C_6H_5)_2C=CHNCH_3$ is a vinylamine derivative which would be tautomeric with $(C_6H_5)_2CHCH=NCH_3$. This would naturally form, on hydrolysis, diphenyl acetaldehyde and methylamine,¹ and not benzophenone and dimethylamine.

The evidence that the product of the alkamine rearrangement is methylimino benzophenone lies in the identification of the hydrolysis products of the latter, benzophenone and methylamine, and in the identification of the reduction product as diphenylmethyl methylamine, $(C_6H_5)_2CHNHCH_3$. The results of Lenth and Stillson make it likely, however, that just as the methylated ring compound is hydrolyzed to benzophenone and dimethylamine, so the unsymmetrical diphenylethylene imine would also be hydrolyzed to benzophenone and methylamine; it might also form the same reduction product as methylimino benzophenone.

It is therefore the three-fold purpose of this investiga-

¹C. W. Lenth, loc. cit.

tion, first, to determine whether the ring compound of Lenth and Stillson is the monomer unsymmetrical diphenylethylene methyl-
imine, $(\text{C}_6\text{H}_5)_2\overline{\text{CCH}_2\text{NCH}_3}$, or some polymer of $\text{C}_{15}\text{H}_{15}\text{N}$; second, to
determine definitely whether the product of the alkamine rear-
rangement is methylimino benzophenone or rather the isomeric di-
phenylethylene imine, $(\text{C}_6\text{H}_5)_2\overline{\text{CCH}_2\text{NH}}$; and, third, in the event that
the alkamine rearrangement product proved to be methylimino benzo-
phenone, to attempt to isolate the postulated intermediate prod-
uct, unsymmetrical diphenylethylene imine.

II. DISCUSSION OF RESULTS

1. Preparation of Unsymmetrical Diphenylethylene Methyl- imine, $(C_6H_5)_2\overline{CCH_2}NCH_3$, and Determination of its Molecular Weight.

In order to prepare pure unsymmetrical diphenylethylene methylimine from the alkamine 2,2-diphenyl-2-hydroxy-ethylamine, $(C_6H_5)_2C(OH)CH_2NH_2$, the methods developed by Stillson¹ were employed. He found that the direct methylation of the alkamine gave a mixture of the monomethyl, dimethyl, and unmethylated alkamine, from which it was difficult to isolate the monomethylated product. To circumvent this difficulty, he prepared the benzene-sulfonyl derivative of the alkamine, 2,2-diphenyl-2-hydroxy-ethyl benzenesulfonamide, $(C_6H_5)_2C(OH)CH_2NHSO_2C_6H_5$, and methylated this compound with methyl sulfate, obtaining 2,2-diphenyl-2-hydroxy-ethyl methyl benzenesulfonamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)SO_2C_6H_5$. Stillson was able to recover the pure monomethylated alkamine, 2,2-diphenyl-2-hydroxy-ethyl methylamine, $(C_6H_5)_2C(OH)CH_2NCH_3$, from its benzenesulfonamide, by treating the latter with metallic sodium in liquid ammonia solution. The methylated alkamine was converted into its benzoyl derivative, 2,2-diphenyl-2-hydroxy-ethyl methyl benzamide, $(C_6H_5)_2C(OH)CH_2N(CH_3)COC_6H_5$; and this compound, when heated with soda-lime, formed unsymmetrical diphenylethylene methylimine, $(C_6H_5)_2\overline{CCH_2}NCH_3$, by losing benzoic acid.

It was found possible to duplicate completely the work of Stillson. The final product, after it had been purified by dis-

¹Loc. cit.

tillation, was an almost colorless oil boiling at 116-118° at a pressure of 6 mm. Molecular weight determinations of this oil corresponded to the empirical formula $C_{15}H_{15}N$. The monomeric structure assigned to the compound is therefore correct.

2. Preparation of Methylimino Benzophenone, $(C_6H_5)_2C=NCH_3$, from Benzophenone and Methylamine, and by the Rearrangement of the Alkamine 2,2-Diphenyl-2-Hydroxy-Ethylamine, $(C_6H_5)_2C(OH)CH_2NH_2$.

Methylimino benzophenone was prepared by the method of Reddelien,¹ from benzophenone anilide, $(C_6H_5)_2C=NC_6H_5$, and methylamine. The benzophenone anilide was formed by the boiling of aniline with benzophenone in the presence of aniline hydrochloride as a catalyst.²

The alkamine was rearranged by being heated for one hour at 150°, or for one-half hour at 275°, in the absence of any rearranging agent. The rearrangement under these conditions was complete.

3. Comparison of the Rearrangement Product with the Product of Reddelien's Synthesis.

Both substances, after they had been purified by fractional distillation, were colorless oils. The rearrangement product boiled at 153-155° at a pressure of 12 mm., and the known methylimino benzophenone distilled at 155-157° at a pressure of 13 mm.

The hydrochlorides, which were precipitated from an anhydrous ether solution of the amines by dry hydrogen chloride, both melted, after recrystallization, at 200-201°; and a mixture of the two had the same melting-point. (Each of them depressed considerably the melting-point of the alkamine hydrochloride,

¹Ber., 54, 3130 (1921).

²G. Reddelien, *ibid.*, 46, 2720 (1913).

which melts at 199°.)

The rearrangement product was reduced with sodium in liquid ammonia solution, and the results of Lenth¹ were completely corroborated. The reduction product is methylamino diphenylmethane, $(C_6H_5)_2CHNHCH_3$. Its nitrate melted at 147°; its hydrochloride melted at 240°, and did not depress the melting-point of the hydrochloride of methylamino diphenylmethane prepared by the reduction of the known methylimino benzophenone. These constants are in agreement with those given by Busch and Leefhelm,² who prepared methylamino diphenylmethane from benzylidene methylamine, $C_6H_5CH=NCH_3$, and phenyl magnesium bromide.

Finally, the indices of refraction of the rearrangement product and of the known methylimino benzophenone were compared. For the redistilled, colorless oils, the values found were $n_D^{20} = 1.6040$ and 1.6045 , respectively. After further purification,³ the two products showed the following refractive indices: for the rearrangement product, $n_D^{20} = 1.6000$; and for known methylimino benzophenone, $n_D^{20} = 1.5998$. From both substances, the hydrochlorides were prepared; they showed the same melting-points as they had previously.

The evidence here presented is considered to show definitely that the alkamine 2,2-diphenyl-2-hydroxy-ethylamine, $(C_6H_5)_2C(OH)CH_2NH_2$, is rearranged by heat to methylimino benzophenone. The possible mechanism of the rearrangement has been discussed by previous workers.⁴

¹Loc. cit.

²J. Prakt. Chem., 77, 22 (1908).

³See Experimental Part, p. 23, for details.

⁴C. W. Lenth, loc. cit.; G. H. Stillson, loc. cit.

4. Rearrangement of the Alkamine and of 2,2-Diphenyl-2-Hydroxy-Ethyl Benzamide, $(C_6H_5)_2C(OH)CH_2NHCOC_6H_5$, by Heat, in the Presence of Soda-lime or Calcium Oxide.

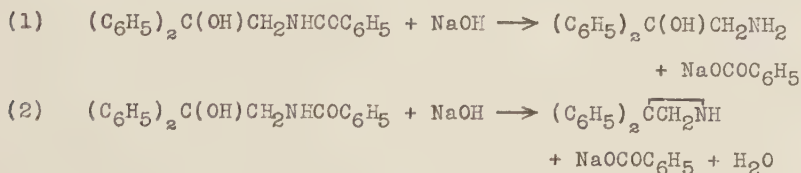
It has been shown that when the alkamine is heated without a rearranging agent, it is converted almost quantitatively into methylimino benzophenone. When, however, the alkamine is heated with calcium oxide, some evidence is found of the presence of a trace of an intermediate product. Under these conditions, for example, the hydrochloride of the rearrangement product melts about ten degrees lower than the hydrochloride of pure methylimino benzophenone, and the melting-point is not raised by repeated recrystallization. A mixture of known pure methylimino benzophenone hydrochloride with the hydrochloride of the rearrangement product melts between the melting-points of the two; and the latter hydrochloride depresses considerably the melting-point of the alkamine hydrochloride.

Furthermore, when phenyl isocyanate is added to the rearrangement product, a slight precipitate is slowly formed. This melts at 220° , and is thought to be the phenylurea of unsymmetrical diphenylethylene imine, $(C_6H_5)_2CCH_2NCONHC_6H_5$. Elementary analysis gives results which correspond closely to the required formula $C_{21}H_{18}ON_2$. Because of the small yields of the substance, however, not enough was ever obtained to permit a thorough study of it. Attempts to hydrolyze small amounts gave no conclusive results.

It was thought likely that the yield of the supposed intermediate might be increased by the heating of the benzoyl derivative of the alkamine, instead of the alkamine itself, with soda-lime or calcium oxide, since Lenth's ring compound is formed from the benzoyl derivative of the methylate alkamine. When

2,2-diphenyl-2-hydroxy-ethyl benzamide, $(C_6H_5)_2C(OH)CH_2NHCOC_6H_5$, is heated with soda-lime at 300° for from five to fifteen minutes, the chief product is the alkamine, of which as much as eighty per cent may be recovered. If the heating is continued for a half-hour or longer, however, none of the alkamine is recovered; the product is methylimino benzophenone, together with some of the supposed unsymmetrical diphenylethylene imine, $(C_6H_5)_2\overline{CCH_2}NH$. The hydrochloride of this mixture shows approximately the same melting-point as that of the mixture obtained from the alkamine and calcium oxide; and neither hydrochloride appreciably depresses the melting-point of the other.

When the mixture of amines is treated with phenyl isocyanate, the yields of the phenylurea describe above are greater than those obtained from the rearrangement product of the alkamine, although still quite small. It was therefore assumed that two reactions take place when the benzoyl derivative of the alkamine is treated with soda-lime--the first a saponification of the benzamide to the free alkamine, which is rapidly rearranged to methylimino benzophenone, with the intermediate formation of unsymmetrical diphenylethylene imine; and the second, a somewhat slower reaction, the direct splitting off of benzoic acid to form the intermediate, which is rearranged to methylimino benzophenone. The reactions are shown below:



Since the rate of formation of methylimino benzophenone from the intermediate is the same in both cases, the fact that

the rearrangement of the benzoyl derivative of the alkamine gives a mixture richer in the presumptive intermediate product than does the rearrangement of the alkamine itself under the same conditions, was explained by the assumption that the benzoyl derivative forms the intermediate more slowly than does the alkamine. When the benzoyl derivative is rearranged, therefore, at the end of half an hour (the minimum time required for an alkamine-free rearrangement mixture), there is more of the intermediate left than there would be if the alkamine itself were rearranged. It was therefore thought that if the saponification of the benzoyl derivative to the alkamine could be suppressed, a greater concentration of the intermediate would be obtained and there would be a better opportunity for its isolation.

5. The Formation of Unsymmetrical Diphenylethylene Benzoylimine, $(C_6H_5)_2\overline{CCH_2}NCOC_6H_5$ (?), by the Thermal Decomposition of 2,2-Diphenyl-2-Hydroxy-Ethyl Benzamide, $(C_6H_5)_2C(OH)CH_2NHCOC_6H_5$.

When the benzoyl derivative of the alkamine is heated without a rearranging agent, visible decomposition begins between 225° and 235° ; but there is only a slight sublimate of benzoic acid. If heating is discontinued after ten minutes, the product contains two substances, which may be separated by fractional crystallization from benzene and ligroin. The less soluble substance is the benzoyl derivative of the alkamine, forty per cent of which may be recovered. The other substance is a solid melting at 134° , which was shown by molecular weight determinations and elementary analysis to have the formula $C_{21}H_{17}ON$, differing from the formula of the benzoyl derivative of the alkamine by one molecule of water. The compound may be obtained almost quantitatively from the benzoyl derivative of the alkamine by heating the latter for fifteen minutes at 300° . For reasons which will

be discussed presently, the substance has been assigned the provisional structure $(C_6H_5)_2\overline{C}CH_2NCOC_6H_5$.

6. Formation of Unsymmetrical Diphenylethylene Benzoylimine, $(C_6H_5)_2\overline{C}CH_2NCOC_6H_5$, from 2,2-Diphenyl-2-Hydroxy-Ethyl Benzanide, $(C_6H_5)_2C(OH)CH_2COC_6H_5$, by the Use of Hydrogen Chloride.

Numerous attempts were made by Lenth¹ to replace the hydroxyl group of the alkamine by a halogen atom, using the tri-bromide, trichloride, and pentachloride of phosphorus, thionyl chloride, hydrogen chloride, hydrogen bromide, and concentrated hydrochloric acid in the presence of zinc chloride. In none of these attempts was he successful. Nevertheless, the hydroxyl group should be easily replaceable, since the alkamine is a tertiary alcohol. Compounds which contain two phenyl groups and a halogen atom bound to the same carbon atom are known, although they are relatively unstable. Diphenylmethyl chloride is easily decomposed by heat;² unsymmetrical diphenylethylene dibromide, $(C_6H_5)_2CBrCH_2Br$, loses hydrogen bromide even at room temperature.³

When the benzoyl derivative of the alkamine is suspended in dry ether (in which it is only slightly soluble), and dry hydrogen chloride is bubbled through the mixture, the precipitate gradually dissolves, leaving a clear solution. If more of the compound is suspended in this solution, and the passage of hydrogen chloride continued, the solution again clears.⁴ Upon evapo-

¹Loc. cit.

²C. Engle and H. Bethge, Ber., 7, 1128 (1874).

³E. Hepp, ibid., 7, 1411 (1874).

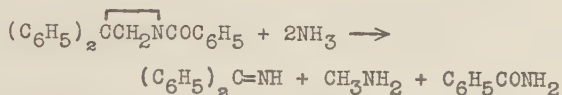
⁴This action was first observed by Dr. G. H. Stillson, and was privately communicated to the author. Mr. G. H. Lovins (Master's Thesis, University of Chicago, 1934) observed the same behavior on the part of 2,2-diphenyl-2-hydroxy-1-methyl ethyl benzanide, $(C_6H_5)_2C(OH)C(CH_3)NHCOC_6H_5$. Because of lack of time neither Stillson nor Lovins studied the nature of the changes.

ration of the ether and the hydrogen chloride, a brown gum is obtained, which gives a positive Beilstein test for halogens, and which, upon recrystallization from 95% alcohol, is converted into the original compound, the benzoyl derivative of the alkamine. When, however, the halogen containing substance is warmed on the steam-bath, there is an evolution of gas, and the residue is identical with the presumptive unsymmetrical diphenylethylene benzoylimine, $(C_6H_5)_2\overline{CCH_2}NCOC_6H_5$, obtained by the thermal decomposition of the benzoyl derivative of the alkamine. No attempt was made to isolate the chlorinated compound, 2,2-diphenyl-2-chloro-ethylbenzamide, $(C_6H_5)_2CClCH_2NHCOC_6H_5$; there is little doubt, however, of its formation.

7. Attempts to Obtain Unsymmetrical Diphenylethylene Imine. $(C_6H_5)_2\overline{CCH_2}NH$, from Unsymmetrical Diphenylethylene Benzoylimine. $(C_6H_5)_2\overline{CCH_2}NCOC_6H_5$.

It was believed that the best evidence of the correctness of the structure of the compound $(C_6H_5)_2\overline{CCH_2}NCOC_6H_5$ would be its conversion into unsymmetrical diphenylethylene imine, $(C_6H_5)_2\overline{CCH_2}NH$, by the removal of the benzoyl group. An acid hydrolysis was not feasible, since the ring product would be easily destroyed by acid. Attempts to remove the benzoyl group by heating the compound with soda-lime, under the same conditions as prevailed during the rearrangement of the benzoyl derivative of the alkamine, yielded neither the ring compound nor methylimino benzophenone, to which the ring compound is supposedly rearranged; instead, an unknown solid compound was obtained, which analysis indicated to be an isomer of the benzoyl derivative of the alkamine. Evidently unsymmetrical diphenylethylene benzoylimine is not an intermediate product in the rearrangement of the benzoyl derivative of the alkamine.

The most likely method removing the benzoyl group without destroying the ring product appeared to be that developed by Stillson, employing liquid ammonia and sodium or sodium amide. It was found that the addition of sodium to a liquid ammonia solution of the benzoylimine, $(C_6H_5)_2\overline{CCH_2NCOC_6H_5}$, caused the reduction of the latter, diphenylmethane being one of the reaction products. Sodium amide does not react with the benzoyl derivative of the ring at the temperature at which the liquid ammonia solution boils; but when the reaction mixture is sealed in a glass bomb tube and allowed to react for fifteen or thirty days, the benzoylimine is converted into benzamide, iminobenzophenone, and presumably methylamine. The latter, however, was not isolated. The course of the reaction is shown below:

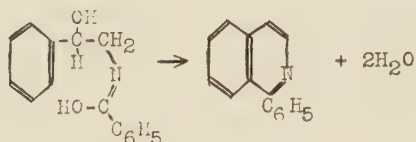


Since it appears, from these results, that any method for removing the benzoyl group from the benzoyl derivative of the ring compound will also destroy the latter, an attempt will be made to prepare the free imine base from its benzyl carbonate derivative, $(C_6H_5)_2\overline{CCH_2NCOOCH_2C_6H_5}$. It is hoped that this compound may be prepared from the benzyl carbonate derivative of the alkamine, $(C_6H_5)_2C(OH)CH_2NHCOCOCH_2C_6H_5$, by the treatment with hydrogen chloride outlined above. The benzyl carbonyl group is easily removed by hydrogen in the presence of palladium, according to the method of Bergmann.¹

8. The Structure of the Compound $C_{21}H_{17}ON$, Melting-point 134° : Unsymmetrical Diphenylethylene Benzoylimine, $(C_6H_5)_2\overline{CCH_2NCOC_6H_5}$.

¹Ber., 65B, 1192 (1932).

There are several products of the composition $C_{21}H_{17}ON$ which might be obtained by the dehydration of 2,2-diphenyl-2-hydroxy-ethyl benzanide. Pictet¹ reports that 2-phenyl-2-hydroxy-ethyl benzanide loses water upon being heated, to form 1-phenyl isoquinoline, as follows:



Since our compound lost only one molecule of water, and since, furthermore, 1,4-diphenyl isoquinoline, which would be the product of such a reaction, would be much more stable toward hydrolysis than is our product, this reaction is ruled out.

Water might be lost with the formation of the compound 2,2-diphenylvinyl benzanide, $(C_6H_5)_2C=CHNHCOC_6H_5$, just as 1,1-diphenyl ethanol, $(C_6H_5)_2C(OH)CH_3$, loses water when heated, forming unsymmetrical diphenylethylene, $(C_6H_5)_2C=CH_2$.² But the vinyl derivative would not form iminobenzophenone on ammonolysis. Even if one molecule of ammonia were added at the double bond, the resulting compound, 2,2-diphenyl-2-amino-ethyl benzanide, $(C_6H_5)_2C(NH_2)CH_2NHCOC_6H_5$, would presumably behave like the closely similar benzoyl derivative of the alkanine, $(C_6H_5)_2C(OH)CH_2NHCOC_6H_5$. The latter is unaffected (except for the removal of the benzoyl group) by sodium or sodium amide in liquid ammonia solution.³ Furthermore, the carbon-carbon linkage in the alkanine derivatives

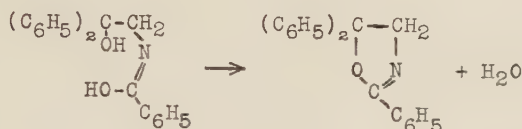
¹Ber., 43, 2384 (1910).

²M. Tiffeneau, Ann. Chim., (VIII) 10, 359 (1907).

³G. H. Stillson, loc. cit.

is rather stable toward both acids and bases: heating the alkanine with hydrochloric acid converts it into diphenyl acetaldehyde, without a loss of carbon, and ammonia;¹ and heating the benzoyl derivative of the alkanine with sodium ethylate at 110° for seven hours causes no cleavage of the carbon-carbon bond.² The compound 2,2-diphenylvinyl benzanide, $(C_6H_5)_2C=CHNHCOC_6H_5$, is tautomeric with diphenyl acetaldehyde benzanide, $(C_6H_5)_2CHCH=NCOC_6H_5$, and should give by ammonolysis benzanide and imino-diphenyl acetaldehyde, and not iminobenzophenone.

A third possible structure for a compound $C_{21}H_{17}ON$ is that of 2,5,5-triphenyl oxazoline, which would be formed as follows:



The compound 2,5-diphenyl oxazoline was prepared by Wolfheim³ from 2-phenyl-2-chloro-ethyl benzanide, $C_6H_5CH(Cl)CH_2NHCOC_6H_5$, by warming the latter with sodium methylate in methyl alcohol. The base was used to favor the formation of the imido-acid tautomer of the substituted benzanide, as well as to neutralize the hydrochloric acid which was formed; but our compound was formed in the absence of any base, and even in the presence of hydrogen chloride. The most serious objection to the oxazoline structure, however, is the ease with which the oxazoline ring is broken: boiling 90% alcohol was sufficient to effect the cleavage of

¹J. E. Cole, loc. cit.

²W. E. Sturgeon, loc. cit.

³Ber. 47, 1447 (1914).

Wolfheims's ring. This cleavage yielded the O-benzoyl derivative of 2-phenyl ethanolamine, $C_6H_5CH(OCOC_6H_5)CH_2NH_2$; and the latter, on treatment with ammonia or sodium hydroxide, was rearranged to the N-benzoyl derivative, $C_6H_5CH(OH)CH_2NHCOC_6H_5$. If our compound were an oxazoline, and it behaved in an analogous manner, then cleavage of the ring in liquid ammonia would yield some derivative of the alkamine; and iminobenzophenone cannot be formed from the latter by sodium amide in liquid ammonia.

The only likely structure for our compound, therefore, is that of unsymmetrical diphenylethylene benzoylimine, $(C_6H_5)_2\overline{CCH_2N-COC_6H_5}$. Only from a compound of this structure could iminobenzophenone be obtained by ammonolysis. It has been shown that the alkamine and its benzoyl derivative show no breaking of the carbon-carbon bond when it is treated with acids in the water system, or with bases in the ammonia or alcohol systems. It is also known that both styreneimine, $C_6H_5\overline{CHCH_2NH}$,¹ and stilbeneimine, $C_6H_5-\overline{CHCH(C_6H_5)NH}$,² upon treatment with dilute acid, undergo cleavage between the nitrogen atom and the carbon atom to which a phenyl group is bound. In the case of the unsymmetrical diphenylethylene imine derivatives, there are two factors tending to weaken the carbon-carbon linkage. The first is the strain imposed by the smallness of the ring; and the second is the weakening of the bond by the linkage of two electronegative phenyl groups, as well as an electronegative nitrogen atom, to one carbon atom. Styreneimine and stilbeneimine are subject to the first strain only; and the alkamine, $(C_6H_5)_2C(OH)CH_2NH_2$, is subject to the equivalent of

¹H. Freundlich and G. Salomon, Zeit. Physik. Chem., A166, 161 (1933); F. Wolfheim, Ber., 47, 1450 (1914).

²A. Darapsky and H. Spannagel, J. Prakt. Chem., (2) 92, 272 (1915); A. Weissberger and H. Bach, Ber., 64B, 1095 (1931).

the second strain alone. Since none of these three compounds undergoes any breaking of the carbon-carbon bond upon treatment with dilute acid or alkali, it is apparent that neither of the two strains is itself sufficient to cause such a cleavage.¹ Only when the two factors operate together, as in the case of Lenth's ring, $(C_6H_5)_2\overline{CCH_2NCH_3}$, and our benzoylated ring, $(C_6H_5)_2\overline{CCH_2NCOC_6H_5}$, is there a hydrolytic splitting of the carbon-carbon bond.

The only evidence against this interpretation is the work of Hoch, which appeared during the course of this research.² He treated propiophenone oxime, $C_2H_5C(NOH)C_6H_5$, with phenyl magnesium bromide, and obtained two bases, $C_{15}H_{15}N$ and $C_{15}H_{17}ON$. To these bases Hoch attributes respectively the structures of 1,1-diphenyl-2-methyl ethyleneimine, $(C_6H_5)_2\overline{CCH(CH_3)NH}$, and of ethyldiphenylmethyl hydroxylamine, $C_2H_5(C_6H_5)_2CNHOH$. A comparison of the following melting-points will show that the latter is really the alkamine 2,2-diphenyl-2-hydroxy-1-methyl ethylamine, $(C_6H_5)_2C(OH)CH(CH_3)NH_2$, of Sturgeon³ and Lovins:⁴

	Hoch	Sturgeon
Base	103°	103-104°
Hydrochloride	258°	246-247°
Benzoyl Derivative	189°	191-191.5°

It will be recalled that Maver⁵ mistook, in the same way, the alkamine 2,2-diphenyl-2-hydroxy-ethylamine, $(C_6H_5)_2C(OH)CH_2NH_2$,

¹At 250° the alkamine hydrochloride is decomposed to benzophenone and dimethylammonium chloride. See C. W. Lenth, loc. cit.

²Compt. rend., 198, 1865 (1934).

³Loc. cit.

⁴Loc. cit.

⁵Loc. cit.

for methyldiphenylmethyl hydroxylamine, $\text{CH}_3(\text{C}_6\text{H}_5)_2\text{CNHOH}$.¹

Hoch obtained his bases after a hydrolysis of the Grignard mixture under conditions which caused the hydrolysis of phenyliminopropiophenone, $\text{C}_2\text{H}_5(\text{C}_6\text{H}_5)\text{C}=\text{NC}_6\text{H}_5$, to aniline and propiophenone. It is doubtful whether a compound with the ring structure assigned by Hoch to the substance $\text{C}_{15}\text{H}_{15}\text{N}$ would survive such conditions unchanged. Hoch based his structure on the following reactions: (1) when heated for twenty hours with 20% hydrochloric acid, the substance was converted into diphenylacetone (unsymmetrical) and ammonium chloride; (2) when reduced with sodium in absolute alcohol, the substance formed 1,1-diphenyl-2-aminopropane, $(\text{C}_6\text{H}_5)_2\text{CHCH}(\text{CH}_3)\text{NH}_2$; and (3) the substance does not react with hydroxylamine or semicarbazide, and is therefore not a ketimine. If the substance had the structure assigned by Hoch, $(\text{C}_6\text{H}_5)_2\text{-}\overline{\text{CCH}(\text{CH}_3)}\text{NH}$, and reacted like the isomeric ring of Lenth $(\text{C}_6\text{H}_5)_2\text{-}\overline{\text{CCH}_2}\text{NCH}_3$, it would be hydrolyzed by warming it for a few minutes with dilute hydrochloric acid, and the products would be benzophenone and ethylammonium chloride. It is our belief that the reactions of Hoch's compound agree perfectly with the behavior to be expected of a compound with the structure of 1-methyl-2,2-diphenyl vinylamine, $(\text{C}_6\text{H}_5)_2\text{C}=\text{C}(\text{CH}_3)\text{NH}_2$. The preparation and study of the latter compound will be undertaken in this laboratory.²

¹J. E. Cole, loc. cit.

²Further attempts are also under way to synthesize unsymmetrical diphenylethylene imine, and to confirm the structure of the compound believed to be its benzoyl derivative.

III. EXPERIMENTAL PART

1. Preparation of the Alkamine 2,2-Diphenyl 2-Hydroxy Ethylamine, $(C_6H_5)_2C(OH)CH_2NH_2$.

Although the preparation of the alkamine has been described by previous workers,¹ the author encountered considerable difficulty in obtaining appreciable yields of the substance by the methods given. The procedure here given was found to give consistently good results.

The apparatus employed consisted of a three-necked one-liter flask fitted with a dropping-funnel, a mercury-seal, and a reflux condenser. To the top of the latter was connected a descending condenser leading to a 500 cc. distilling flask, which was used as a receiver. The two condensers were cooled by separate water supplies. The apparatus was dried thoroughly before the reaction was begun, and every outlet was equipped with a calcium chloride tube.

A Grignard reagent (five moles) was prepared from 27 g. of magnesium and 120 cc. (180 g.) of bromobenzene, in 350 cc. of anhydrous ether, the mixture being stirred continuously from the inception of the reaction. After the reaction had ceased, the flask was immersed in an oil bath, and the reaction mixture was gently refluxed. At the end of an hour, the water supply of the reflux condenser was shut off, and the temperature of the oil bath gradually increased. When the bath was between 160° and 165°, the color of the Grignard reagent changed from brown to

¹M. E. Maver, loc. cit.; J. E. Cole, loc. cit.

gray-green, and white fumes began to fill the system. At this point, approximately 250 cc. of ether had been removed by distillation. As soon as the color change occurred, water was again sent through the reflux condenser, and heating was discontinued. The dropping-funnel was replaced by an "oxime-gun" of the type described by Cole² and by Lovins,³ and 30 g. (one mole) of dry, powdered acetophenone oxime was added to the Grignard mixture. The reaction was violent; considerable heat was evolved, and if the oxime was added too rapidly, charring occurred. The reaction was accompanied by the evolution of white fumes; it was observed that some of this white smoke hovered in the reflux condenser, furnishing by its position a convenient gage of the speed with which the oxime could be added. Rapid stirring was maintained throughout the reaction, and was continued until all of the oxime had reacted and a smooth mixture was obtained.

This mixture was decomposed by pouring it into ice and dilute hydrochloric acid, the total volume being kept as small as possible (about one liter). The benzene layer was removed, and the acid solution was extracted twice with the ether which had been recovered during the concentration of the Grignard reagent, and then once more with fresh ether. To the cold acid solution was then added one-half pound of ammonium nitrate, which was dissolved by vigorous stirring of the solution. The nitrate of the alkamine was precipitated immediately in the form of fine yellow needles. After the chilled solution had stood for half an hour, in order to permit coagulation of the precipitate, the mixture was filtered with suction, and the precipitate, without being

²Loc. cit.

³Loc. cit.

washed, was sucked as dry as possible.

The nitrate was transferred to one liter of hot water (not boiling), and as much as possible dissolved by stirring. When a uniform suspension had been obtained, an excess of concentrated sodium hydroxide solution was added to it, and the mixture cooled as quickly as possible. The alkamine was precipitated immediately in the form of cream-colored, plate-like crystals. The cold mixture was filtered with suction, and the alkamine (which contained a little magnesium hydroxide) was washed with water and then dissolved in hot 95% alcohol. The alcoholic solution was filtered by gravity, the precipitated magnesium hydroxide washed with hot alcohol, and the alkamine recovered from the combined alcoholic filtrates by the addition of an excess of water. When dried, the product was light yellow in color, and melted at 109-110°. It was pure enough for the preparation of the benzoyl derivative; when the pure alkamine was required, it was recrystallized from chloroform by the addition of ligroin. The yield was usually about 35-40%.

2. Preparation of Unsymmetrical Diphenylethylene Methyl-
imine, $(C_6H_5)_2CCH_2NCH_3$, and Determination of its Molecular Weight.

The laboratory procedure in the preparation of the methylated ring was the same as that described by Stillson.¹ The benzenesulfonyl derivative of the alkamine, $(C_6H_5)_2C(OH)CH_2NHSO_2C_6H_5$, was methylated with methyl sulfate; and from the product the methylated alkamine, $(C_6H_5)_2C(OH)CH_2NHCH_3$, was recovered by the removal of the benzenesulfonyl group with sodium in liquid ammonia. The benzoyl derivative² of the methylated alkamine, $(C_6H_5)_2C(OH)CH_2N(CH_3)COC_6H_5$, was heated with calcium oxide in order to

¹Loc. cit.

²Ibid.

form the ring compound,¹ $(C_6H_5)_2\overline{CCH_2NCH_3}$. The latter, after it had been purified by fractional distillation, boiled at 116-118° at a pressure of 6 mm. The molecular weight of the compound was determined by the Rast method,² by the lowering of the melting-point of camphor:

.0145 g. of oil dissolved in .1841 g. of camphor
lowered the melting-point 15.5°

.0460 g. of oil dissolved in .3431 g. of camphor
lowered the melting-point 24.8°

Calculated for $C_{15}H_{15}N$, 209. Found, 203, 216.

3. Preparation of Methyliminobenzophenone, $(C_6H_5)_2C=NCH_3$.³

A mixture of 27 g. of benzophenone and 28 g. (two moles) of aniline was boiled for twenty minutes in an Erlenmeyer flask, together with 1.5 g. of aniline hydrochloride. The aniline had been previously purified by being refluxed with zinc and sodium hydroxide and then distilled. After the mixture had cooled, 120 cc. of absolute alcohol was added to it. Crystallization began in a short time, and proceeded rapidly. The product, phenylimino benzophenone, after recrystallization from 95% alcohol, formed yellow crystals (20 g.) which melted sharply at 113°.

In a small distilling flask immersed in an oil bath, 4 g. of the phenylimino benzophenone and 0.5 g. of aniline hydrobromide were heated to 225°, and methylamine was bubbled through the molten mixture. The methylamine was dried by passage through powdered sodium hydroxide. After an hour, during which the temperature was maintained at 220-230°, 1.5 g. of aniline had distilled from the mixture. The residue was fractionally distilled, and the portion boiling between 145° and 165° at about 15 mm.

¹Ibid.; C. W. Lenth, loc. cit.

²Ber., 55, 1051 (1922).

³G. Reddelien, ibid., 46, 2720 (1913); 54, 3130 (1921).

collected. This was redistilled, and one gram of colorless methyliminobenzophenone obtained at 155-157° and 13 mm. For this substance, $n_D^{20} = 1.6045$. The hydrochloride was precipitated by dry hydrogen chloride from an anhydrous ether solution of the amine; it was recrystallized from absolute alcohol by the addition of anhydrous ether. The melting-point of the hydrochloride was 200-201°, and was not changed by recrystallization.

Lenth¹ reported that the hydrochloride of methylimino benzophenone, when prepared in this manner, disappeared in a few minutes. It has been the author's experience that if the ether is slightly wet, the precipitated hydrochloride extracts the moisture from the ether and forms an almost invisible, colorless solution, which settles to the bottom of the vessel or clings to its walls, and may be easily overlooked. If this happens, the crystalline hydrochloride may be recovered by immediate decantation of the ether, solution of the residual liquid in absolute alcohol, and addition of dry ether to the alcoholic solution.

In order further to purify the methylimino benzophenone, the hydrochloride, together with an excess of powdered sodium hydroxide, was suspended in dry ether, and the mixture shaken for one hour. The precipitate was removed by a suction filter, and the ether solution distilled. The amine had the same boiling-point as before; but $n_D^{20} = 1.5998$.

4. Rearrangement of the Alkamine, $(C_6H_5)_2C(OH)CH_2NH_2$, to Methyliminobenzophenone.

The alkamine (7 g.), in a small distilling flask, was heated for one hour in an oil bath maintained at 140-150°. (At temperatures between 250° and 300°, the reaction is completed in half an hour.) The product, methylimino benzophenone, was dis-

¹ Loc. cit.

tilled at a reduced pressure, and five grams collected which boiled at 158-162° and 15 mm. This was redistilled; most of it boiled at 153-155° at a pressure of 12 mm. The distillate was colorless, and gave $n_D^{20} = 1.6040$. The chloroplatinate of the oil was prepared by the addition of a 10% absolute alcohol solution of chloroplatinic acid to an absolute alcohol solution of the imine; sufficient anhydrous ether was added to cause precipitation. The product was brought on a filter, washed well with anhydrous ether, and dried over sodium hydroxide in a vacuum desiccator. Analysis for platinum:

3.755 mg. of sample gave .910 mg. of Pt.
4.848 mg. of sample gave 1.176 mg. of Pt.

Calculated for $C_{28}H_{28}N_2PtCl_6$: 24.39%

Found: 24.22%, 24.26%

The hydrochloride of the imine was prepared in the manner described above for the synthetic imine. After recrystallization, it melted at 200-201°, and did not depress the melting-point of the synthetic methylimino benzophenone hydrochloride. When the imine was recovered from the hydrochloride as described previously, it gave $n_D^{20} = 1.6000$. The hydrochloride was analyzed for chlorine by the Mohr method:

.1731 g. of sample required 7.20 cc. of .1042 N. $AgNO_3$

Calculated for $C_{14}H_{14}NCl$, 15.31%; found, 15.36%

5. Hydrolysis of the Rearrangement Product.

The rearrangement product (.5 g.) was warmed for ten minutes with dilute hydrochloric acid (6 N.); after the mixture had cooled, it was extracted with ether. From the residue of the ether extract an oxime was prepared. It melted at 139-140°, and did not depress the melting-point of known benzophenone oxime.

The hydrochloric acid solution of the methylamine produced was evaporated to dryness, and the residue recrystallized

from absolute alcohol and ether. The chloroplatinate was prepared and analyzed:

2.300 mg. of sample gave .950 mg. of Pt.
2.046 mg. of sample gave .849 mg. of Pt.

Calculated for $C_2H_{12}N_2PtCl_6$, Pt: 41.36%;

Found, Pt: 41.30%; 41.49%

6. Reduction of the Rearrangement Product.

To 35 cc. of liquid ammonia in an unsilvered Dewar flask were added 1 g. of the hydrochloride of the rearrangement product and .3 g. (three moles) of sodium. The mixture was stirred by bubbling ammonia through it, and the amine, which had been precipitated as an amorphous mass, gradually dissolved. After the solution had evaporated to dryness, water was added to the residue, and the mixture extracted twice with ether. The ether solution was dried with anhydrous sodium sulfate, and then decanted from the latter. When dry hydrogen chloride was passed through the ether solution, a gum was precipitated; after several recrystallizations from alcohol and ether, this yielded a crystalline product which melted at 239-240°, and which did not depress the melting-point of the hydrochloride of known methylaminodiphenylmethane, $[(C_6H_5)_2CHNH_2CH_3]^+ Cl^-$, prepared by the reduction of synthetic methylimino benzophenone. The nitrate, precipitated by the treatment of the amine with a small amount of water and a few drops of concentrated nitric acid, melted at 145°. Busch and Leefhelm¹ give the melting-point of methylaminodiphenylmethane nitrate as 142°.

7. Rearrangement of 2,2-Diphenyl-2-Hydroxyethylbenzamide,

$(C_6H_5)_2C(OH)CH_2NHCOC_6H_5$, by Heat in the Presence of Soda-lime.

Powdered soda-lime (5 g.) was placed in a small round-

¹Loc. cit.

bottomed, long-necked flask, and heated for an hour in a metal bath maintained at 300°. The benzoyl derivative of the alkamine (5 g.) was then added to it in powdered form, and the heating continued for the required length of time, care being taken to exclude moisture. The mixture was then cooled, extracted repeatedly with anhydrous ether, the ether removed from the combined extracts by distillation, and the residue distilled at reduced pressure.

When the benzoyl derivative of the alkamine was heated in the above manner for fifteen minutes or less, the product distilled between 140° and 160° at a pressure of 25 mm., and solidified in the receiver. After being washed with anhydrous ether, the substance melted at 110°, and did not depress the melting-point of the known alkamine. The identification of the product as regenerated alkamine was completed by a comparison of the hydrochlorides (M.P. 199°) and of the phenyl-ureas (M.P. 160°, sintering from 150°). The yield of recovered alkamine was as high as 80%.

8. Unsymmetrical Diphenylethylene Imine (?), $(C_6H_5)_2\overline{CCH_2}NH$, and its Phenyl Urea, $(C_6H_5)_2\overline{CCH_2}NCONHC_6H_5$.

When the benzoyl derivative of the alkamine was heated for thirty minutes or longer, the product distilled at 165-170° at a pressure of 20 mm. It was a yellow oil, and the yield was about two grams. The hydrochloride of this product, after several recrystallizations, melted at 189-192°, and this melting-point was not appreciably changed by further recrystallization of the salt. It depressed considerably the melting-point of the alkamine hydrochloride (M.P. 199°); but it depressed only slightly the melting-point of synthetic methylimino benzophenone hydrochloride (M.P. 200°), the melting-point of the mixture lying between 192° and 200°.

Although the oil obtained in this way was converted by acid hydrolysis into benzophenone and a methyl ammonium salt, the oil was not wholly methyliminobenzophenone. The latter does not react with phenyl isocyanate; but when the rearrangement product was sealed with phenyl isocyanate, a precipitate began to form within a few minutes. At the end of an hour, the reaction appeared to be complete. The mixture generally did not solidify completely; usually there was only a sediment of fine crystals. The sealed tube was broken open, and absolute alcohol added to its contents in order to remove the excess of phenyl isocyanate. When the odor of the latter had completely disappeared, a few drops of chloroform and an excess of ligroin were added to the mixture. The precipitate was collected on a filter, and recrystallized twice from pyridine and ligroin, then triturated with chloroform and ligroin. The urea melted at 220° , with previous sintering; the melting-point was not changed by recrystallization of the compound. The substance was only slightly soluble in chloroform, benzene, alcohol, ether, and carbon tetrachloride; it dissolved readily in pyridine and warm dioxane. The yield varied from 10 mg. to 50 mg. of purified product. The substance was thought to be N-phenyl N'-unsymmetrical diphenylethylene urea, $(C_6H_5)_2\overline{CCH_2NCONHC_6H_5}$. It was analyzed for nitrogen:

4.664 mg. of sample gave .377 cc. of N_2
at 25° and 740.7 mm. (corr.)

5.723 mg. of sample gave .464 cc. of N_2
at 23° and 746.4 mm. (corr.)

3.991 mg. of sample gave .327 cc. of N_2
at 24.5° and 746.4 mm. (corr.)

Calculated for $C_{21}H_{18}ON_2$, N: 8.92%;

Found, N: 8.85%, 9.00%, 9.03%

Analysis of the compound for carbon and hydrogen by the Pregl method gave results which did not consistently check the

theoretical values; the latter, calculated for $C_{21}H_{18}ON_2$, are 5.8% for hydrogen and 80.2% for carbon. Of ten analyses, the results ranged from 78.1% to 80.2% for carbon, seven of them lying between 78.4% and 78.8%; for hydrogen, the values ranged from 5.6% to 6.8%, six of them lying between 5.9% and 6.4%.

The urea is evidently not carbanilide, $(C_6H_5NH)_2CO$, which melts at 235° ; the latter contains 73.6% of carbon, 5.7% of hydrogen, and 13.2% of nitrogen.

9. Thermal Decomposition of 2,2-Diphenyl-2-Hydroxy-Ethyl Benzamide, $(C_6H_5)_2C(OH)CH_2NHCOC_6H_5$, to Unsymmetrical Diphenyl-ethylene Benzoylimine, $(C_6H_5)_2CCH_2NCOC_6H_5$.

The benzoyl derivative of the alkamine (12 g.) was placed in an open Erlenmeyer flask immersed in a metal bath heated to 300° . After a few moments, the melted mass visibly decomposed; water vapor was evolved, together with a small amount (about 20 mg.) of benzoic acid, which condensed on the upper walls of the flask. The benzoic acid was identified by its melting-point (121°); it did not depress the melting-point of known benzoic acid.

After fifteen minutes, heating was discontinued. The product was cooled and dissolved in 20 cc. of hot 95% alcohol. It crystallized from the alcohol in large, pale yellow monoclinic crystals, which were not completely decolorized by several recrystallizations from alcohol and bone-black. Recrystallization from chloroform and ligroin, however, gave small white crystals which melted sharply at 134° . These were analyzed:

15.327 mg. of sample gave .626 cc. of N_2
at 26° and 749.5 mm. (corr.)

8.359 mg. of sample gave .344 cc. of N_2
at 24° and 749.0 mm. (corr.)

4.097 mg. of sample gave 2.208 mg. of H_2O
and 12.627 mg. of CO_2

4.315 mg. of sample gave 2.372 mg. of H_2O
and 13.320 mg. of CO_2

Calculated for $C_{21}H_{17}ON$:		Found
N:	4.68%	4.53%, 4.57%
H:	5.73%	6.05%, 6.15%
C:	84.25%	84.05%, 84.19%

The molecular weight of the substance was determined by the lowering of the melting-point of camphor. Results:

.0196 g. of sample dissolved in .4044 g. of camphor
caused a lowering of 6.50°.

.0125 g. of sample dissolved in .2304 g. of camphor
caused a lowering of 7.80°.

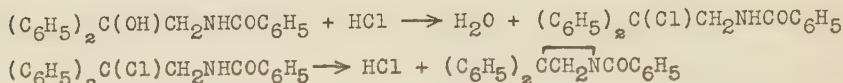
Calculated for $C_{21}H_{17}ON$, 299; found, 298, 279.

10. Formation of Unsymmetrical Diphenylethylene Benzoyl-
imine by the Action of Hydrogen Chloride on 2,2-Diphenyl 2-Hydroxy-
Ethyl Benzamide.

The benzoyl derivative of the alkamine (.4 g.) was suspended in anhydrous ether (50 cc.) in a deep test-tube, and dry hydrogen chloride was bubbled through the mixture in a slow, steady stream. After about three hours, the precipitate had disappeared. A small amount of the benzoyl derivative of the alkamine was added to the clear solution; in a few minutes, it had also been dissolved. After the ether had been driven off on a steam bath, a yellow gum remained. This gave a positive Beilstein test; but when it was attempted to recrystallize the gum by solution in 95% alcohol, the original benzoylated alkamine was obtained (by hydrolysis of the chloride represented by the gum in impure form). The recovered product melted at 180-182°, and did not depress the melting-point of known 2,2-diphenyl-2-hydroxy-ethyl benzamide (M.P. 183°).

When the gummy residue was heated on the steam-bath, there was an evolution of tiny gas bubbles. After the substance had been warmed for thirty minutes, the product was recrystallized

twice from 95% alcohol. It now melted at 130-132°, and did not depress the melting-point of known unsymmetrical diphenylethylene benzoylimine (M.P. 134°). The following reactions evidently occur:



11. Attempts to Obtain Unsymmetrical Diphenylethylene, $(\text{C}_6\text{H}_5)_2\overline{\text{CCH}_2}\text{NH}$, from its Benzoyl Derivative, $(\text{C}_6\text{H}_5)_2\overline{\text{CCH}_2}\text{NCOC}_6\text{H}_5$.

The benzoyl derivative of the ring compound (5 g.) was heated at 300° for thirty minutes with an equal amount of previously ignited soda-lime. The cooled residue was extracted repeatedly with 15 cc. portions of dry ether, the extracts combined, and the ether removed by evaporation at reduced pressure. A white solid residue was left, which, after recrystallization from chloroform and ligroin, formed silky white needles (2 g.) which melted sharply at 144-145°.

3.021 mg. of sample gave .120 cc. of N_2
at 25° and 745.0 mm. (corr.)

2.949 mg. of sample gave .111 cc. of N_2
at 24° and 744.0 mm. (corr.)

Found, N: 4.39%, 4.22%

The analyses correspond to the formula $\text{C}_{21}\text{H}_{19}\text{O}_2\text{N}$ (4.42% of N_2), which is that of some isomer of the benzoyl derivative of the alkamine. The substance was not investigated further.

From the soda-lime residue, 860 mg. of benzoic acid was recovered. This amount corresponds to the saponification of 2.5 grams of the starting material. Nevertheless, when the ether washings of the solid described above were treated with dry hydrogen chloride, only a trace of any hydrochloride was precipitated. From a hydrochloric acid trap which had been used to catch any

volatile amines, a small amount of ammonium chloride was obtained. This was identified by Nessler's test.

When the saponification with soda-lime was attempted at 150° instead of 300°, the same products were obtained. In neither case could the alcohol, aldehyde, or ketone which corresponded to the ammonia evolved, be isolated or identified.

An attempt was made to remove the benzoyl group with sodium in liquid ammonia. The benzoyl derivative of the ring compound (1 g.) was dissolved in liquid ammonia, and a little more than the theoretical amount of sodium was added. The solution turned momentarily blue, then orange, and finally deep red. The ammonia was allowed to evaporate, and the residue extracted with dry ether. In the ether extract, no amine could be detected. The only identifiable products were benzamide and an oil which had a pleasant aromatic odor, which gave a positive aluminium chloride test for aromatic hydrocarbons, and which boiled at 260° (uncorr.). It was believed to be diphenylmethane.

Since the ring appeared to have been reduced by sodium, an attempt was made to saponify the benzoyl derivative with sodium amide. An excess of the latter was added to a solution of .5 g. of the benzoylimine in 200 cc. of liquid ammonia in an open Dewar flask, and the solution was allowed to evaporate. The residue was extracted with dry ether; from the ether extract 450 mg. of the starting substance was recovered. There was no evidence of any other compound.

Finally, an attempt was made to effect the saponification with sodium or potassium amide and liquid ammonia in a bomb tube. Several methods were employed. In one, metallic potassium (1 g.) was dissolved in 10 cc. of liquid ammonia, a rusty iron wire being used as a catalyst, and when the solution had become colorless,

one gram of the powdered benzoylimine was added. This was washed down the sides of the tube with 15 cc. of liquid ammonia, and the tube was sealed after being thoroughly chilled in a carbon dioxide ice and acetone bath. Under these conditions, the saponification was completed in two weeks, as was evidenced by the fact that benzamide was the only solid compound recovered in the ether extract of the residue. When, however, 7.5 g. of the benzoylimine was sealed with four grams of sodium amide and 25 cc. of liquid ammonia, the reaction was incomplete even after thirty days, 4.5 grams of the starting material being recovered. This difference in results may have been due either to the greater activity of potassium amide, or to the fact that the sodium amide employed was not freshly prepared.

After the bomb had been allowed to stand at room temperature for the desired length of time, it was thoroughly chilled as before, and then the tip broken. The ammonia was boiled off by raising the tube gradually, so that the surface of the ammonia was about an inch above the level of the bath. In this way, a rapid rate of evaporation was maintained, with no danger of boiling-over. When all of the ammonia had been removed, the residue was extracted repeatedly with dry ether, and the ether extracts filtered with suction and combined. The ether solution was evaporated to dryness at reduced pressure, in order to remove any dissolved ammonia. The residue was then redissolved in cold ether, and the ether solution shaken three times with 40 cc. portions of a mixture of chopped ice and 2 M. hydrochloric acid. The ether layer contained benzamide, if the original reaction had gone to completion; or a mixture of benzamide and the benzoylimine. The benzamide was identified by its melting-point (129°) and the fact that it did not depress the melting-point of known benzamide.

The cold hydrochloric acid solution was made alkaline with sodium hydroxide, and the basic solution extracted twice with ether. The combined ether extracts were washed twice with ice-water, and then dried with anhydrous sodium sulfate.

Through some of this ether solution, dry hydrogen chloride was passed. The hydrochloride which precipitated, after recrystallization from absolute alcohol and ether, sublimed without melting between 270° and 290° . The hydrochloride of iminobenzophenone is reported as decomposing, without melting, above 250° .¹ From the hydrochloride a chloroplatinate was prepared.

3.594 mg. of sample gave .914 mg. of Pt.
3.701 mg. of sample gave .933 mg. of Pt.

Calculated for $C_{26}H_{24}N_2PtCl_6$, Pt: 25.26%

Found, Pt: 25.43%, 25.21%

Some of the hydrochloride was warmed for a few minutes with 10 cc. of 2 M. hydrochloric acid, and the mixture extracted with ether. The ether was evaporated, and from the residue an oxime was prepared. This melted at $138-140^{\circ}$, and did not depress the melting-point of known benzophenone-oxime (M.P. $140-141^{\circ}$). The hydrochloric acid solution was evaporated to dryness on the steam-bath, and from the residue, which was assumed to be ammonium chloride, a chloroplatinate was prepared.

2.581 mg. of sample gave 1.129 mg. of Pt.
2.619 mg. of sample gave 1.152 mg. of Pt.

Calculated for $N_2H_8PtCl_6$, Pt: 43.96%

Found, Pt: 43.74%, 43.98%

In order to make perfectly sure of the identity of the compound iminobenzophenone, some of the ether solution containing the latter was evaporated, and phenyl isocyanate added to the

¹G. E. P. Smith, Jr., and F. W. Bergstrom, J. Am. Chem. Soc., 56, 2095 (1934).

residual oil. An immediate reaction ensued, with the evolution of heat. The product, after recrystallization from hot 95% alcohol, melted at 162-163°. The reported melting-point of the phenyl-urea of iminobenzophenone is 160-162°. ¹ On hydrolysis with boiling dilute acid, the urea gave benzophenone, which was identified by the melting-point of its oxime; an ammonium salt, which was identified by Nessler's test; and an aniline salt, which was identified by the bleaching-powder test.

The benzoyl derivative of iminobenzophenone was obtained by the shaking of an ether solution of the imine with an excess of sodium hydroxide solution, and the gradual addition of benzoyl chloride. The derivative melted, after recrystallization from 95% alcohol, at 118°. The reported melting-point is 117-118°. ²

Finally, the picrate of iminobenzophenone was prepared by the addition of a saturated ether solution of picric acid to an ether solution of the amine. The picrate settled out in yellow needles, which melted, when they had been thoroughly washed with dry ether, at 170°. Thomas ³ reports the melting-point as 170°; but Smith and Bergstrom ⁴ report it as 281-282°. A picrate was made from some iminobenzophenone prepared by Mr. Alfred Ingle from benzonitrile and phenyl magnesium bromide. The picrate melted at 170°, and did not depress the melting-point of our picrate.

¹Ibid.

²G. Reddelien and H. Danilof, Ber., 54B, 3132 (1921).

³Arch. Pharm., 243, 395 (1905); Chem. Zentral., 1905 (2), 555.

⁴Loc. cit.

SUMMARY

1. Stillson's synthesis of the ring compound unsymmetrical diphenylethylene methylimine, $(\text{C}_6\text{H}_5)_2\overline{\text{CCH}_2\text{NCH}_3}$, was repeated, and the substance was shown, by molecular weight determinations, to be monomeric.

2. The product of the rearrangement, by heat alone, of the alkamine 2,2-diphenyl-2-hydroxy-ethylamine, $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})\text{CH}_2\text{NH}_2$, was shown definitely to be methylimino benzophenone, $(\text{C}_6\text{H}_5)_2\text{C}=\text{NCH}_3$. The rearrangement product was compared with synthetic methylimino benzophenone as to the boiling-points, the refractive indices, the reduction products, and melting-points of the hydrochlorides of the two substances, and all the properties were shown to be identical.

3. The product of the rearrangement of the alkamine or of its benzoyl derivative, in the presence of soda-lime, was shown to contain traces of an amine which reacts with phenyl isocyanate to form a compound $\text{C}_{21}\text{H}_{18}\text{ON}_2$. This amine is believed to be unsymmetrical diphenylethyleneimine, $(\text{C}_6\text{H}_5)_2\overline{\text{CCH}_2\text{NH}}$, the postulated intermediate in the alkamine rearrangement; and its addition product with phenyl isocyanate is believed to have the structure $(\text{C}_6\text{H}_5)_2\overline{\text{CCH}_2\text{NCONHC}_6\text{H}_5}$.

4. The thermal decomposition of the benzoyl derivative of the alkamine was shown to yield a dehydration product with the formula $\text{C}_{21}\text{H}_{17}\text{ON}$. Evidence is presented that this compound is the benzoyl derivative of the ring compound unsymmetrical diphenylethyleneimine, $(\text{C}_6\text{H}_5)_2\overline{\text{CCH}_2\text{NCOC}_6\text{H}_5}$.

5. A method is presented for replacing the hydroxyl group of the alkanine with a halogen atom. The preparation of the benzoyl derivative of the ring compound from the benzoyl derivative of the alkanine, through the intermediate formation of the compound 2,2-diphenyl-2-chloro-ethylbenzamide, $(C_6H_5)_2C(Cl)-CH_2NHCOC_6H_5$, is described.

6. Attempts to obtain unsymmetrical diphenylethyleneimine from its benzoyl derivative by the use of heat and soda-lime, sodium in liquid ammonia, and sodium amide in a liquid ammonia bomb, are described.

7. The work of Hoch, which contradicts in some degree the work done in this laboratory on substituted ethyleneimines, is reviewed, corrected, and reinterpreted.

In conclusion, the author wishes to express his deep appreciation to Professor Stieglitz for the inspiration and guidance which have made this work possible; and to Dr. R. W. Johnson for his many helpful suggestions.

